Effect of chemical treatment on the mechanical and thermal properties of hemp fibre reinforced thermoset sandwich composites

M.M. Kabir, H. Wang, F. Cardona & T. Aravinthan
Centre of Excellence in Engineered Fibre Composite (CEEFC), Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland 4350, Australia.

ABSTRACT: In this study hemp-thermoset sandwich composites were prepared by using unsaturated polyester resin. To improve fibre matrix adhesion alkalization and acetylation treatment on the fibres were carried out. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to investigate the changes of fibres chemical constituents after treatment. Mechanical properties such as flexural strength, flexural modulus and strain at break of untreated and treated fibre composites were studied and compared. The incorporation of the alkalized fibres resulted in composites better flexural properties and 8% treatment showed best results. Thermal stability of the fibre was also enhanced for the treated fibre. In general, thermal and mechanical properties of the treated fibre and its composites were superior to the untreated fibres.

1 INTRODUCTION

Increasing environmental awareness throughout the world has impacted on materials design and engineering. Introduction of natural fibres from annually renewable resources to be used as reinforcement in composites provides benefits to the environment with respect to the degradability and utilization of natural materials (Rout et al. 2001). Natural fibres such as jute, flax, hemp, coir, sisal etc. are used as reinforcing fibres in thermoset and thermoplastic matrix. The attractive features of these fibres are their low cost, light weight and high specific modulus in contrast to the synthetic fibres (Ray et al 2001).

Hemp fibre (*Cannabis sativa*) is one of the plant fibres known as bast fibre recently gaining the attention to be used as diversified reinforcing applications in engineering composite materials to be used as structural parts. Although, most of the natural fibres cellulose acts as a main structural component, lignin, and hemicelluloses also play an important role in determining the characteristics properties of the fibre. Therefore, major limitation of using this fibre in high strength composite applications is poor adhesion characteristics with the polymeric matrix and dimensional instability. This results in poor mechanical properties of the composite materials. The natural fibre is hydrophilic while matrix materials are hydrophobic. As a result, there is an inherent incompatibility between hydrophilic fibre and hydrophobic resin.

The approximate chemical composition of hemp fibre is: cellulose (70.2-74.4%), hemicelluloses (17.9-22.4%), lignin (3.7-5.7%), pectin (0.9%) and waxy substances (0.8%) (Mohanty et al. 2000). Moisture from the atmosphere comes in contact with the fibres hydrophilic hydroxyl groups form new hydrogen bonds with water molecules. Therefore, pectin and waxy substance hold these water molecules and hindering free hydroxyl groups to react with polar matrix. As a result, ineffective/poor bonding between hydrophobic resin and hydrophilic fibre occurs. This problem can be overcome by treating these fibres with suitable chemicals to decrease the hydrophilic hydroxyl group in the fibres. Chemical treatment such as alkalization and acetylation reacts with hydrophilic hydroxyl groups of natural fibre and improves hydrophobic characteristics and facilitates better bonding with matrix materials. Several authors used alkalization and acetylation treatments on natural fibres to improve its composites mechanical and thermal properties. Leonard et al. (2007) used 0.16%NaOH treatment on hemp fibre for 48 hrs and found treated composites had 30% and 50% tensile and shear strength properties. Viviana et al. (2004) showed 4% higher thermal stability of hemp fibre after 8% NaOH treatment. Bledzki et al. (2008) used different concentration of acetylation treatment on flax fibres and reported 18% acetylation treatment showed 25% higher tensile and flexural properties.

Hemicellulose of hemp fibre is sensitive to the action of NaOH, acetic acid and acetic anhydride

which also reacts with the lignin and cellulosic compounds (Sinha & Rout, 2009). As a result, hydrophilic tendency of the fibre reduced and improved fibre matrix adhesion characteristics of the composites. These studies have been focused on the alkalization and acetylation treatment on hemp fibres to investigate the changes (removal of hemicelluloses, lignin and cellulosic constituents) of chemical activity of the fibre with temperature. DSC and TGA analysis were carried out on fibre to evaluate the degree of chemical changes occurred by the use of different treatments. Short and randomly oriented hemp fibre was reinforced in polyester matrix to develop core material and hemp fabric was used as a skin to prepare sandwich composites. The effect of chemical treatment on the fibre was investigated to determine the degree of adhesion between the fibre and matrix through mechanical property analysis. Experimental three point bending tests were carried out in order to compare the flexural stiffness and the load-carrying capacity of these composites containing untreated and treated fibres.

2 EXPERIMENTAL

2.1 *Materials*

Hemp fibres were obtained from Eco Fibre Industries and hemp fabrics were collected from Hemp Resources Limited, Australia. General purpose unsaturated polyester resin was used as matrix and methyl ethyl keton peroxide was used as a curing catalyst.

2.2 *Fibre surface treatments*

Hemp fibres were soaked with NaOH solution of varying concentrations of 4%, 6%, 8% and 10% for 3 hours at room temperature followed by washing with distilled water for several times to leach out the absorbed alkali. The fibres were dried at room temperature for 8 hours followed by oven dried at 100°C for 6 hours.

Alkali pre-treated hemp fibres were soaked in acetic acid and subsequently treated with acetic anhydride at room temperature for 3 hours. After that fibre was washed with distilled water several times to remove the residual acetic anhydride.

(a) (b)

Figure 1. (a) Fibre orientation in the mold; (b) skin attach on the core.

2.3 *Composites processing*

Manufacturing process of sandwich composites are presented in Figure 1. Initially, fibres were chopped into 3-6 mm in length and randomly spread in a mold. Figure 1(a) shows fibre orientation in the mold. Extreme care was taken to get uniform distribution. Polyester resin and catalyst was mixed with the weight ratio of 1:0.015 and spread over the fibres to get maximum possible fibre matrix wetting. A simple hand lay-up technique was used to prepare core materials. Prepared core was kept in room temperature for 6 hours followed by oven drying at 80°C for 5 hours. Afterwards, hemp fabrics were used at both side of the core material and polyester resin was used to adhere between the surfaces. Figure 1(b) shows the skin and core orientation for sandwich composite preparation.

3 TEST METHODS

3.1 *Differential scanning calorimetry (DSC)*

DSC measurements were performed by using a (DSC Instrument, Model No. Q100) thermal analyser. The fibres were taken between 6 to 10mg for analysis. The samples were heated up at a rate of 10°C/min from 10 to 450°C in a nitrogen environment purged at 20ml/min. Each fibre was analysed separately and overlapped for comparison.

3.2 *Thermogravimetric analysis (TGA)*

TGA analysis of fibres was conducted by thermal gravimetric analyser (TGA-Model No. Q500). The fibres samples were taken between 6 to 10 mg for analysis. The samples were heated up steadily at a rate of 10°C/min from 25 to 500°C in helium medium (60 ml/min). Each fibre was analysed separately and overlapped for comparison.

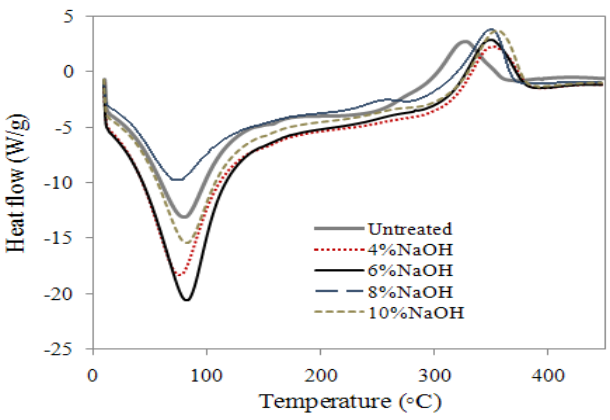

Figure 2. DSC analysis of alkali treated fibre

3.3 *Flexural test*

The flexural test was performed by using a computer controlled universal testing machine of 10KN load cell. The ASTM D-790 test method was followed and a span to depth ratio of 16:1 was maintained. The cross-head speed of 2mm/min was applied. At least five specimens of each composite were used and reported the average values. Flexural modulus (E_f) and flexural strength (σ_f) were calculated by using equations:

$$E_f = \frac{PL^3}{4wt^3y} \quad (1)$$

$$\sigma_f = \frac{3PL}{2wt^2} \quad (2)$$

Where P is the applied load, w and t are the width and the thickness of the specimen respectively, L is the support span length and y is the deflection of the centre of the specimen. The values of strain at break of the composites were calculated using equation:

$$Strain at break(\%) = \frac{\sigma_f}{E_f} X\,100 \quad (3)$$

4 RESULTS AND DISCUSSION

Hemp/polyester sandwich composites with 10 wt% of fibre loading were prepared to investigate the effect of alkalization and acetylation on fibres thermal properties and its composites mechanical properties like flexural strength, flexural modulus and strain at break (%).

4.1 *DSC analysis of fibres*

DSC analysis enables to identify the chemical activity occurring in the fibre as heat was applied (Sinha & Rout, 2009). Figure 2 shows the thermal response of the untreated and alkali treated hemp fibre as a function of temperature. Both untreated and treated fibres exhibited one broad endothermic peak between the temperature of 70-90°C and one exothermic peak between 260-380°C. The first endothermic peak corresponded to the evaporation of moisture absorbed by the fibre. In this region some variations of thermal energy was observed with the effect of different concentration of alkali treatment. This was due to the changes of moisture absorbed by the fibres after treatment (Ray et al. 2002).

The region between 110-200°C shows no exothermic or endothermic changes reflected that the fibres were thermally stable. It was reported that for natural fibres lignin degrades at the temperature around 200°C while the other constituents such as hemicelluloses and α-cellulose degrades at higher temperature (Aziz & Ansell, 2004). Therefore, the peak exothermic in Figure 2 corresponded to the decomposition of lignin, hemicelluloses and α-cellulose of the fibre. For untreated fibre, lignin, hemicelluloses and α-cellulose degradation exothermic peak was observed between the temperature ranges of 260-370°C. While all treated fibres showed exothermic peak between 300-385°C. This was presumably due to the partial removal of lignin, hemicelluloses and α-cellulose from the fibre with the effect of NaOH treatment and more temperature was required to remove these constituents. As a result, thermal stability of the treated fibres was increased compared to the untreated fibre. In addition to this, hydrophobicity of

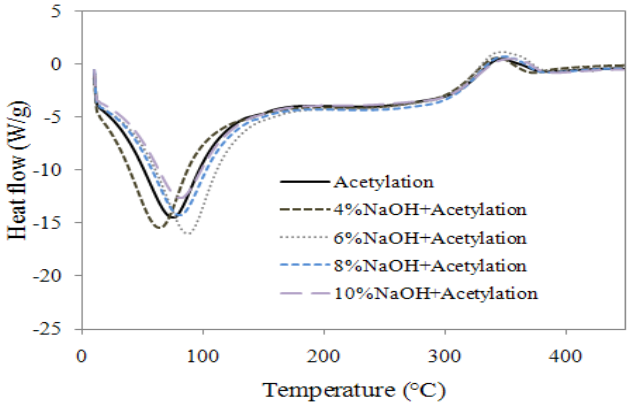

Figure 3. DSC analysis of acetylation treated fibre

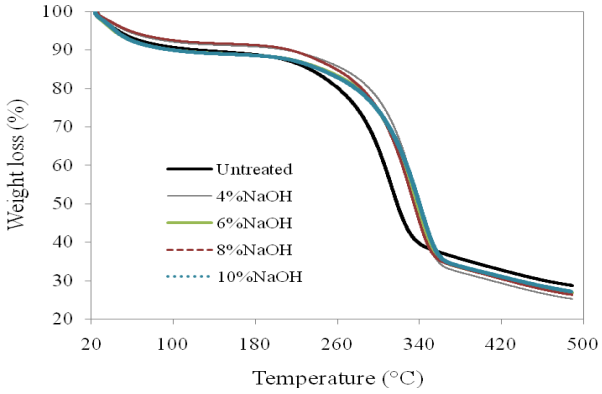

Figure 4. TGA analysis of alkali treated fibre

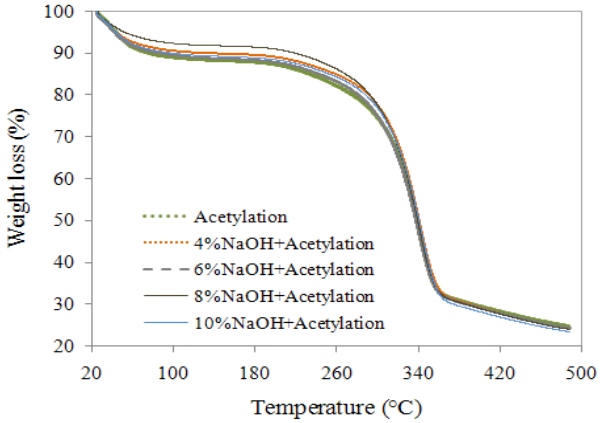

Figure 5. TGA analysis of acetylation treated fibre

Table 1. Themogravimetric analysis on hemp fibre with different chemical treatment

Fibre treatment		Alkalized fibre		Acetylated fibre	
		2nd stage thermal degradation (hemicelluloses and lignin)	3rd stage thermal degradation (cellulosic components)	2nd stage thermal degradation (hemicelluloses and lignin)	3rd stage thermal degradation (cellulosic components)
		Tempt range 200-300°C	Tempt range 320-400°C	Tempt range 200-300°C	Tempt range 320-400°C
Untreated		270	331	288	354
NaOH treated	4%	289	354	295	356
	6%	287	353	290	354
	8%	290	350	292	355
	10%	288	357	291	357

the fibre was increased as the tendency of water molecules hold by the lignin and hemicelluloses were reduced. From Figure 2 it was observed that 8%NaOH treated fibre showed higher thermal stability compared to other treated fibres which indicates improved hydrophobic nature of the fibre and higher adhesion possibility with the matrix.

Figure 3 shows DSC analysis curve for acetylation (alkali pre-treated) treated hemp fibres. In this case, all the fibres showed similar exothermic peak between 300-375°C for decomposition of lignin, hemicelluloses and α-cellulose. As a result, thermal degradation characteristics for the alkali pre-treated acetylated fibres were similar to each others. This was due the acetylation treatments caused further purification of the fibre after alkali treatment and minimized the variations of degradation temperature. From this analysis, it can be deduced that the treated hemp fibre is more thermally stable compared to the untreated fibre since the untreated hemp fibres have lower decomposition temperature.

4.2 *TGA analysis of fibre*

TGA analysis was carried out to observe the distinct process of weight loss occurring on fibres at different temperatures. Figure 4 shows three stages of weight loss process with prolonged temperatures. From the curve, the first stage of weight loss started from 30-110°C was due to the release of moisture content by the fibre. The second stage major degradation occurred with the temperature range at about 200-300°C, which was related to the degradation of lignin and hemicelluloses of the fibre. The last stage of weight loss temperature ranges at about 340-380°C, indicates the degradation of α-cellulose and other non cellulosic materials from the fibre (Pracella et al. 2006).

It was examined that untreated hemp fibre started degrading at 200°C. However, this value increased for the alkali treated fibres and displayed higher thermal stability of the fibre. This was evidenced by the degradation rate of the treated fibre with higher temperature and by lowering the weight loss compared to the untreated fibre. This might be caused by the alkali treatment which reduced the hemicelluloses and lignin content of the fibre. As a result fibres became more hydrophobic and enhanced the better possibility to adhere with the matrix.

Figure 5 shows the TGA curves for acetylated (alkali pre-treated) fibres. The degradation behaviours for all the treated fibres were similar to each other. Moreover, the weight loss variations as a function of temperature were also minimized after acetylation treatment. This can be attributed to the further purification of the fibres were take place due to the treatment. From Table 1 it was observed that, in all cases the degradation temperatures of lignin, hemicelluloses and cellulosic constituents for acetylated fibres were higher than the untreated and alkalized fibres. As a result, it can be deduced that acetylated fibres were more thermally stable than the untreated and alkalized fibres.

Table 2. Flexural properties of the sandwich composites

Type of reinforcing fibre		Alkalized fibre composites			Acetylated fibre composites		
		Flexural strength (MPa)	Flexural Modulus (GPa)	Strain at break (%)	Flexural strength (MPa)	Flexural Modulus (GPa)	Strain at break (%)
Untreated		47.50	3.50	1.33	44.46	3.78	1.17
NaOH treated	4%	48.80	3.60	1.35	48.15	3.54	1.36
	6%	55.83	3.65	1.53	51.65	3.44	1.49
	8%	60.51	4.44	1.36	53.31	4.00	1.36
	10%	60.01	4.37	1.37	51.43	3.60	1.42

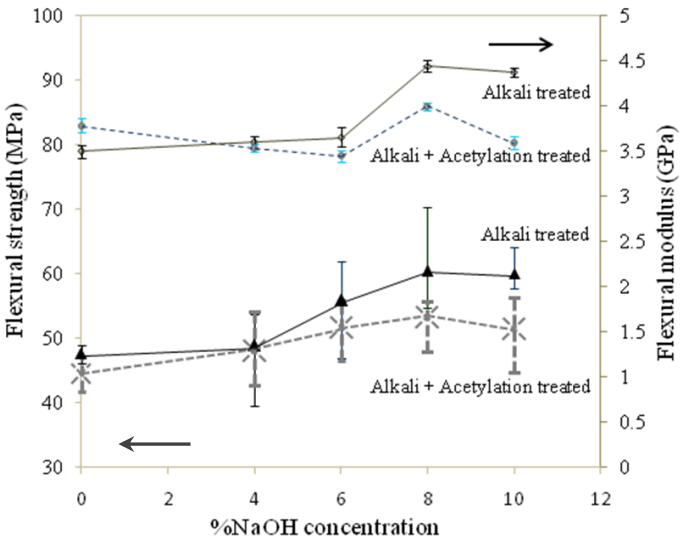

Figure 6. Flexural properties of the composites

4.3 *Flexural properties of the composites*

Flexural properties of untreated and treated hemp fibre reinforced polyester sandwich composites are shown in Figure 5 and Table 2. The flexural strength and modulus for all the alkali treated fibre composites were increased compared to the untreated fibre composites. At higher concentration such as 6%, 8% and 10% NaOH treated composites showed 15%, 22% and 21% improvement in strength and 5%, 22% and 20% improvement in modulus properties. This was possibly due to the removal of hemicelluloses, lignin and cellulosic constituents from the fibre after alkali treatment. As a result fibres became more hydrophobic and increased adhesion at the interface between the fibre and matrix. Several authors reported similar observations on improved flexural strength properties after alkalization of reinforcing fibres (Mwaikambo & Ansell, 2002, Sreekala et al. 1997).

On the other hand, acetylated (alkali pre-treated) composites showed steady improvement on strength properties with higher concentration of NaOH. However, in all cases alkali treated composites showed better flexural property performance compared to the acetylated composites (Gulati & Sain, 2006). Therefore, the strength performance of treated and untreated fibre composites showed subsequent improvement from 4 to 8% NaOH concentration. Afterwards, the pattern changed and tendency of strength properties were fall down at 10%NaOH concentration. The reason for lowering the property was presumably due to the excess delignification (removal of cementing materials) of fibre occurred at higher concentration of NaOH (Mishra et al. 2002). This resulted lowering the fibre strength and degrades composite properties.

From Table 2 it is observed that, alkali treated composites strain at break were increased compared to the untreated composites. This was related to higher fibre matrix adhesion with the effect of alkali treatment. However, acetylated fibre composites exhibited lower elongation at break compared to all other composites. This was because of the acetylation treatment made fibre more brittle in character. Similar observations also reported by others (Khalil et al. 2000).

5 CONCLUSIONS

- Two different surface modification methods (alkalization and acetylation) were applied on hemp fibre. Alkali treatment removes hemicelluloses, lignin and cellulosic constituents from the fibre and became more thermally stable than untreated fibres. Acetylation treatment on alkali pre treated hemp fibres caused further purification on the removal of hemicelluloses, lignin and cellulosic components from the fibre after alkali treatment. The thermal degradation behaviours of acetylated fibres were more uniform than the alkali treated fibres.
- Alkali treated fibre composites have higher flexural properties and 8%NaOH treatment showed best results. In this case flexural strength and modulus were improved by 22%. The possible reason for this improvement is the alkalization helps to improve fibres hydrophobicity by removing hemicelluloses, lignin and other cellulosic matters from the fibre. As a result compatibility between the fibre and hydrophilic resin were improved which resulted superior mechanical properties.
- Flexural properties of acetylated fibre composites showed lower values compared to the alkalized composites. This was due to the brittle characteristics of the fibre with the effect of acetylation treatment. Strain at break for acetylated fibre composite was lower than untreated fibre composites also supports these results.
- From the above discussion it can be stated that, chemical treatments on hemp fibres achieved some degree of success in improving the fibre matrix adhesion, mechanical properties and thermal properties of the fibres and composites. This method of fibre modification will help to develop natural fibre sandwich composites with better performance under load bearing conditions.

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